CVWB Conclusion #1: "The physical-chemical data for fipronil and its degradates is accurate and complete."

Overall Comments: The physicochemical data for fipronil and fipronil degradates appears to be accurate and mostly complete based on information provided within Section 2. However, the authors should address the specific comments below to help clarify several uncertainties and enhance the overall dataset.

Specific Comments:

Section 3, pg. 3: Similar to the remaining sections of this report, please insert an opening paragraph that summarizes the available physicochemical data and, more importantly, addresses the potential sources of variability (which, in some cases, span orders of magnitude) observed within certain parameters for fipronil, fipronil-sulfide, fipronil-sulfone, and fipronil-desulfinyl. For example, the $K_{oc}s$ for fipronil range from 396 to 37,154 L/kg. Without providing a discussion, it's unclear whether these discrepancies are a result of differences in study quality or experimental conditions (e.g., soil type, temperature, pH, etc.).

Section 3, pgs. 4-5: Within the opening paragraph of Section 3, please clarify the justification for calculating geometric means — especially considering that these means do not reflect the significant amount of variability for certain parameters. In addition, it would be useful to indicate whether these geometric means are ultimately considered or used for deriving water and sediment quality criteria. If not, then please delete the geometric means, as these numbers are a bit misleading.

Section 3, pg. 5: Octanol-water partitioning coefficients (K_{ow}) for fipronil degradates were not provided since experimental data were not available. However, two out of four fipronil K_{ow} s provided were based on predictions by the BioByte Bio-Loom program. Therefore, using BioByte Bio-Loom or another program (e.g., US EPA's EPISuite), predicted K_{ow} s for fipronil degradates should be provided to ensure that the dataset is complete. Otherwise, if the authors have concluded that experimental K_{ow} s are only valid for this report, then fipronil K_{ow} s derived from Tomlin 1997 and Donovan and Pescatore 2002 should be deleted.

Section 3, pgs. 6-8: If geometric means are calculated for other parameters, then geometric means should be calculated and included for hydrolysis, aqueous photolysis, aerobic biodegradation, and anaerobic biodegradation half-lives included within Table 2.

CVWB Conclusion #2: "Ecotoxicity data screening resulted in a high quality (relevant and reliable) data set for criteria derivation and did not result in removal of pertinent high quality data from the data set used for criteria derivation."

2a. "Ecotoxicity data used for criteria derivation with control survival <90% did not bias the calculated criteria."

2b. "Use of toxicity values for field collected organisms with acclimation period less than 48 hours did not bias the calculated criteria."

Overall Comments: The study rating system did result in high-quality data, and the use of data with control survival <90% or acclimation periods <48 hours likely did not introduce significant bias when calculating criteria. However, as discussed below, a more important question and concern is whether, as a result of the study rating system used, the calculated criteria are biased as a result of discarding ~70% of usable data points. An additional concern is that the majority of toxicity data used to calculate criteria were derived from one study by Weston and Lydy 2014.

Specific Comments:

Section 4, pg. 9: Both subsections on wildlife LC_{50} and NOEC values should be moved to Section 5, as the UDCM rating system is not discussed until Section 5. In addition, wildlife toxicity data represent a subset of ecotoxicity data, so it's unclear why discussion of these data is separate from the other ecotoxicity data.

Sections 5-6, pgs. 9-11: Although the UCDM and UCDSM study rating system appears to be a reasonable and scientifically defensible approach for identifying and relying on high-quality toxicity data for water/sediment quality criteria, this rating system is too stringent for prioritizing data within this report, as toxicity data for fipronil and fipronil degradates are relatively sparse compared to other well-studied pesticides (e.g., atrazine). Therefore, by only relying on certain "relevant and reliable (RR)" toxicity data as the basis for calculating criteria, the authors have, in addition to 14 studies rated as not relevant, disregarded the vast majority of usable data - i.e., approximated or less sensitive RR data as well as "supplemental" studies that were rated as "relevant and less reliable (RL)", "less relevant and reliable (LR)", or "less relevant and less reliable (LL). If included, these additional data may have resulted in different water/sediment quality criteria based on the methods used within Section 7. For example, it appears as though the majority of discarded data for fipronil was within the range of 1-100 ug/L (this can also be seen as a large gap within Figure 4), raising questions about whether inclusion of these data would have resulted in a different fit of the Burr Type III distribution to the cumulative frequency curve. In addition, there are also concerns that the majority of RR data used to calculate criteria were derived from one study by Weston and Lydy 2014, raising questions about whether this study is adequately representative of other available toxicity studies.

Moreover, as a result of only relying on certain RR data, the authors were also forced to use assessment (i.e., safety) factors for some criteria calculations since toxicity data were limited (which was a direct result of discarding data) — an approach that may have introduced more uncertainty vs. relying on all usable data in the absence of assessment factors. Indeed, in some cases, the authors were unable to calculate criteria since requirements for taxa-specific data and assessment factor procedures were not met following data reduction. To address this concern, the authors should consider comparing existing criteria within the report with criteria that are calculated based on the full data set (RR, RL, LR, and LL) without the use of assessment factors (assuming taxa-specific data requirements are met).

Below is a table that summarizes the number and percent of excluded RR, RL, LR, and LL data relative to the full RR + supplemental dataset; data points were summed for each group and compound based on information provided within the data tables provided at the end of the report. As shown below, ~70% (157/224) of usable data points (RR, RL, LR, and LL) were discarded as a result of the rating system used within this report.

| Criteria | Compound | RR data points used for criteria calculation | Excluded RR data points | Supplemental (RL, LR, LL) data points (acute + chronic) | Total data points (acute + chronic) | Percent of data discarded |
|----------|----------------------|--|----------------------------|--|--|---------------------------|
| Water | Fipronil | 20 acute 3 chronic | 8 acute 6 chronic | 56 | 93 | 75% (70/93) |
| | Fipronil-sulfide | 10 acute 1 chronic | 5 acute 0 chronic | 6 | 22 | 50% (11/22) |
| | Fipronil-sulfone | 18 acute 2 chronic | 13 acute 5 chronic | 10 | 48 | 58% (28/48) |
| | Fipronil-desulfinyl | 2 acute 1 chronic | 6 acute 7 chronic | 5 | 21 | 86% (18/21) |
| | Fipronil-carboxamide | 1 acute 0 chronic | 0 acute 0 chronic | 0 | 1 | 0% (0/1) |
| Sediment | Fipronil | 2 acute 0 chronic | 6 acute 0 chronic | 2 | 10 | 80% (8/10) |
| | Fipronil-sulfide | 2 acute 1 chronic | 7 acute 0 chronic | 1 | 11 | 72% (8/11) |
| | Fipronil-sulfone | 2 acute 0 chronic | 7 acute 0 chronic | 1 | 10 | 80% (8/10) |
| | Fipronil-desulfinyl | 2 acute 0 chronic | 5 acute 0 chronic | 1 | 8 | 75% (6/8) |
| | TOTAL | 59 acute 8 chronic | 57 acute 18 chronic | 82 | 224 | 70% (157/224) |

CVWB Conclusion #3: "The acute water quality criteria, if attained, are likely to protect aquatic organisms from harmful physiological effects that result from short-term exposures to fipronil and/or its degradates and the criteria calculated are technically valid. The acute water quality criteria are unlikely to be either under- or overprotective."

3a. "The acute criteria derived via assessment factors, described below, result in criteria that are valid and protective and are not overly conservative."

Overall Comments: The acute water quality criteria are likely to be protective of aquatic organisms. However, as discussed above, there are concerns that, as a result of discarding the vast majority of usable data, the criteria may be overprotective – especially considering that the acute criteria for fipronil-sulfide (0.62 ng/L) and fipronil-sulfone (1.3 ng/L) are below current analytical detection limits for both compounds. Likewise, as a direct result of discarding data, the use of assessment factors may have led to overprotective criteria (vs. relying on usable data in the absence of assessment factors).

Specific Comments:

Section 7.1.1, pg. 11 and Section 7.1.3, pg. 16: Only the 5th percentile at the 50% confidence limit was used for calculating criteria. Therefore, it's unclear why the other estimates (5th percentile at the 95% confidence limit, and 1st percentile at the 50% and 95% confidence limit) were

reported, as this may create unnecessary confusion among readers. Recommend deleting or inserting a statement providing justification for including these numbers within the report.

Section 7.1.1., Figure 4 and Section 7.1.3, Figure 6: Please add minor tick marks to the x- and y-axis so it's easier to estimate the 5th percentile by hand. In addition, please change the scale of the y-axis to 0.01 to 1 since no data points are below 0.01.

CVWB Conclusion #4: "The chronic water quality criteria, if attained, are likely to protect aquatic organisms from harmful physiological effects that result from long-term (i.e., any long period or a duration that covers a substantial portion of an organism's life span) exposures to fipronil and/or its degradates and the criteria calculated are technically valid."

4a. "The chronic water quality criteria derived via acute-to-chronic ratios are valid and protective and are not overly conservative."

Overall Comments: The chronic water quality criteria are likely to be protective of aquatic organisms. However, as discussed above, there are concerns that, as a result of discarding the vast majority of usable data, the criteria may be overprotective – especially considering that the chronic criteria for fipronil (3.2 ng/L), fipronil-sulfide (0.14 ng/L), and fipronil-sulfone (0.17 ng/L) are near or below current analytical detection limits for all three compounds. Likewise, as a direct result of discarding data, the use of ACRs may have led to overprotective criteria (vs. relying on usable data in the absence of ACRs).

Specific Comments:

Section 7.2.1, pgs. 18 and 19: Please delete " μ g/L" for the D. magna SMACRs, as both of these numbers are unitless.

CVWB Conclusion #5: "The interim acute bioavailable sediment quality criteria were conservatively derived and denote a concentration protective of the most sensitive aquatic life while highlighting data gaps and future studies needed for more robust analysis. Due to the limitations on available data and remaining uncertainty in the UC Davis Sediment Criteria Derivation Methodology, the interim acute bioavailable sediment quality criteria should not be utilized as regulatory values."

5a. "The interim acute bioavailable sediment quality criteria for fipronil and its degradates are not recommended to be utilized as regulatory values because they may be overly conservative because the data available only account for two species, one of which is known to be particularly sensitive to fipronil and degradates based on the aqueous data sets, and when few data are available the derivation method is conservative to account for cases in which it is unknown whether the available species are relatively sensitive."

Overall Comments: The interim acute bioavailable sediment quality criteria are likely to be protective of aquatic organisms. However, as discussed above, there are concerns that, as a

Reviewer: David C. Volz, University of California, Riverside **Date Review Submitted:** February 6, 2017

result of discarding the majority of usable data, the interim criteria may be overprotective – especially considering that the criteria for fipronil (4.2 ng/g), fipronil-sulfide (3 ng/g), and fipronil-sulfone (2 ng/g) are near or below the current analytical detection limits for all three compounds.

Specific Comments:

Section 8.1.4, pg. 23: Since all other interim acute BSQCs are reported at ng/g OC, please add one more line that converts the interim acute BSQC for fipronil-desulfinyl from 1.2 ug/g OC to 1200 ng/g OC.

CVWB Conclusion #6: "The interim chronic bioavailable sediment quality criteria were conservatively derived and denote a concentration protective of the most sensitive aquatic life while highlighting data gaps and future studies needed for more robust analysis. Due to the limitations on available data and remaining uncertainty in the UC Davis Sediment Criteria Derivation Methodology, the interim chronic bioavailable sediment quality criteria should not be utilized as regulatory values."

6a. "The interim chronic bioavailable sediment quality criteria for fipronil and its degradates are not recommended to be utilized as regulatory values because they may be overly conservative because the data available only account for two species, one of which is known to be particularly sensitive to fipronil and degradates based on the aqueous data sets, and when few data are available the derivation method is conservative to account for cases in which it is unknown whether the available species are relatively sensitive."

Overall Comments: The interim chronic bioavailable sediment quality criteria are likely to be protective of aquatic organisms. However, as discussed above, there are concerns that, as a result of discarding the majority of usable data, the interim criteria may be overprotective – especially considering that the criteria for fipronil (0.7 ng/g), fipronil-sulfide (0.4 ng/g), and fipronil-sulfone (0.3 ng/g) are below the current analytical detection limits for all three compounds.

Specific Comments:

Section 8.2.4, pg. 25: Since all other interim chronic BSQCs are reported at ng/g OC, please add one more line that converts the interim chronic BSQC for fipronil-desulfinyl from 0.20 ug/g OC to 200 ng/g OC.

CVWB Conclusion #7: "The water quality criteria were not adjusted based on water quality effects, specific ecotoxicity data, or effects in other environmental compartments; the derived criteria are scientifically sound and technically valid based on the available information on these topics."

Overall Comments: The water quality criteria have adequately considered the available information about bioavailability, mixtures, water quality effects, etc.

Specific Comments:

Section 11.1, pg. 31: Within the second paragraph, the authors state that a default BMF of 1 was used yet a BMF of 10 is within the $NOEC_{water}$ equation toward the bottom of the page. Since 1250/321 = 3.89, this is presumably a typo within the equation and needs to be corrected.

CVWB Conclusion #8: "The assumptions, limitations, and uncertainties regarding derivation of the water quality criteria are accurate and include all factors that significantly affect the resulting criteria."

Overall Comments: The authors should insert a section that addresses the potential uncertainty associated within discarding usable data. Ideally, the authors should consider comparing existing criteria within the report with criteria that are calculated based on the full data set (RR, RL, LR, and LL) without the use of assessment factors (assuming taxa-specific data requirements are met). Based on the results of this comparison, the authors should then quantify this uncertainty and discuss how inclusion/exclusion of data points alters the calculated criteria.

CVWB Conclusion #9: "The acute and chronic water quality criteria are appropriate to protect aquatic organisms in the entire Central Valley of California, including the Sacramento River and San Joaquin River Basins as well as the Tulare Lake Basin."

Overall Comments: Given that the calculated water quality criteria are in the low ng/L range, it is unlikely that fipronil and fipronil degradates will negatively impact aquatic organisms within the entire Central Valley of California if these criteria are met.

"The Big Picture"

- (a) "In reading the Draft Water Quality Criteria Report, are there any additional scientific issues that should be part of the scientific portion of the water quality criteria derivation that are not described above? If so, comment with respect to the derivation of water quality criteria."
- (b) "Taken as a whole, are the scientific portions of the water quality criteria derivations based upon sound scientific knowledge, methods, and practices?"

Overall Comments: As discussed above, the authors may have introduced significant bias in the calculated criteria by discarding ~70% of usable data points. Therefore, the authors should systematically address the potential uncertainty associated with inclusion/exclusion of data. The authors should also acknowledge and address the shortcomings of using certain criteria that are near or below current analytical detection limits in water and sediment. In other words, how will it be possible to benchmark water and sediment concentrations if certain criteria are below current analytical detection limits? What if fipronil and fipronil degradates are not detected within water and sediment samples? Would this still be a cause for concern for aquatic organisms?